

Luminescence of Europium β -diketonates with
Derivatives of 1,10-Phenanthroline

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The luminescence, excitation of luminescence, UV and IR absorption spectra of a number of europium β -diketonates of compositions $\text{Eu}(\beta)_3\text{Ph}$, $\text{Eu}(\beta)_3\text{nH}_2\text{O}$ and $\text{Eu}(\beta)_4\text{Na}$ were examined. β – the row consisting of nine β -diketonates with increasing acceptor properties, from dipivaloylmethane (DPM) to hexafluoroacetylacetone (HFAA). Ph – phenanthroline derivatives: 3,4,7,8-tetramethyl-phenanthroline, 5-methyl-phenanthroline, phenanthroline, 5-phenyl-phenanthroline, 4,7-diphenyl-phenanthroline, 5-nitro-phenanthroline. Spectra of $\text{Eu}(\beta)_3\text{Bpy}$ (Bpy – H-, or D-2,2'-bipyridine) were investigated also.

Our interest to the spectroscopy of the europium β -diketonates was induced by the perspective of use of these compounds in layered organic multilayer light emitting diodes (OLEDs). A row of important characteristics of these materials influencing the intensity of the electroluminescence such as stability of compounds, mobility of the charge carriers and height of the potential barriers for charge carrier injection is correlated with donor-acceptor properties of the substituents in ligands. From the other side, these donor-acceptor properties influence location and intensity of bands of ligands and Ln^{3+} ions in the absorption and luminescence spectra, vibration frequencies and electron-phonon interaction, energy transfer and quantum yield of luminescence. This work is continuation of our experimental investigations on spectroscopy of europium β -diketonates [1-4].

The introduction of the substituents with different donor-acceptor properties in molecules of β -diketone or phenanthroline changes a distribution of the π -electronic density in them as well as effective charges on the oxygen and nitrogen atoms. This leads to the changes of the bond strengths and distances “metal-ligand”. Influence of the effective charges of atoms in the nearest surroundings of Eu^{3+} as well as the size of ligands on spectroscopic characteristics was investigated.

During the synthesis of some compounds $\text{Eu}(\text{DPM})_3\text{Ph}$ a photochemical reaction was observed, analogous to [5]. A two-stage photochemical reaction in solution of europium acetate or other salt with 1,10-phenanthroline had been observed there. At the second, reversible stage of the reaction, an intense green dyeing of the reaction products was observed. This photochemical reaction hindered formation of the complexes, in particular, $\text{Eu}(\text{DPM})_3\text{Nphen}$. The dependencies of the parameters of the reversible photochemical reaction on the phenanthroline derivatives was investigated.

The efficiency of the excitation of Eu^{3+} through ligand's bands, Stark splitting of the Eu^{3+} energy levels, relative intensities of the Eu^{3+} electronic transitions, vibration frequencies, patterns of intensity distribution in the vibronic sidebands and their dependencies on variation of the ligand's substituents were examined.

To determine the energies of ligand levels the luminescence and excitation of luminescence spectra of gadolinium compounds were studied. Competition

of the ligand donor-acceptor properties and steric factor was examined as in the row of β -diketonates, so in the row of the phenanthroline derivatives. Three rows of the compounds $\text{Eu}(\beta)_3\text{Ph}$ with different donor-acceptor properties of the β -diketonates: DPM (strong donor), FOD (has one donor radical and other acceptor radical), TTFA (strong acceptor) were studied. The influence of the steric factor dominates in the row of the $\text{Eu}(\text{DPM})_3\text{Ph}$ compounds. Correlation of the spectra and the structure with the donor-acceptor properties of the Ph was observed in the row of the $\text{Eu}(\text{TTFA})_3\text{Ph}$ adducts.

It was demonstrated that in compounds with two type ligands the influence of donor properties of substituents in one type of ligands on Stark splitting of Eu^{3+} levels and on the strength of electron-phonon interaction is equivalent to the influence of the acceptor properties of the substituents in the second type of ligands.

It was show how the most stable compounds with optimal characteristics of luminescence can be selected using variation of substituents in both ligands. Values of the luminance of adducts were measured and analysed. It was demonstrated that fluorinated europium β -diketonates containing phenyl derivatives of phenanthroline exhibit the highest luminance. Possible mechanisms of the excitation energy decay as well as mechanisms of energy transfer from the ligands to the europium ions are discussed.

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